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A PHASE EQUILIBRIUM STUDY OF THE SYSTEM
n-OCTANE – WATER – PROPIONIC ACID[1]

BY A. I. JOHNSON, W. F. FURTER, AND T. W. BARRY

ABSTRACT

In this work the phase equilibrium relationships of the system *n*-octane – water – propionic acid were investigated. The vapor–liquid boiling point curves for the binary systems *n*-octane – propionic acid and water – propionic acid at atmospheric pressure were established by means of a modified Colburn still. Analysis of the bottoms and condensed distillate was accomplished by titration with standard base. The reliability of the vapor–liquid data was checked by means of an activity coefficient plot. The three-component solubility data at 25°C. were determined by the "synthetic" method. Tie-line data were obtained by analysis of conjugate solutions. Using the method of Scheibel and Friedland, the distribution curve was predicted from the ternary solubility curve and the vapor-liquid data of the two binary systems. The predicted curve agreed quite well with the experimentally determined curve.

INTRODUCTION

A review of the literature has revealed that relatively few binary and ternary systems have been compared with respect to phase equilibrium relationships.

The system *n*-octane – propionic acid – water was chosen for study over several other as yet uninvestigated systems. The systems *n*-octane – propionic acid and water – propionic acid proved to be miscible in all proportions, as opposed to other binary systems tested.

LIQUID–VAPOR EQUILIBRIUM STILL

For this work the binary system liquid–vapor curves were determined with a modified Colburn still shown in Fig. 1. Larger residue and distillate chambers than those specified by Colburn were used to permit a greater contact between the vapor from the flash boiler and the liquid in the residue chamber. The chambers each held about 40 ml. of liquid. The general design and mode of operation is the same as that described by Jones, Schoenborn, and Colburn (1).

Titration of the propionic acid in each pipetted sample with standard base was found to be a satisfactory method of analysis.

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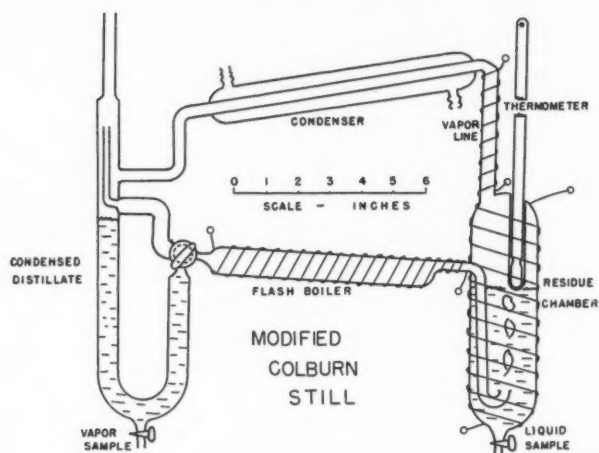
FIG. 1.   Vapor–liquid equilibrium still.

The Colburn still was further modified to use a thermometer instead of a thermocouple. The thermometer was calibrated from the boiling points of water, *n*-octane, and propionic acid.

DETERMINATION OF VAPOR–LIQUID DATA OF BINARY SYSTEMS

The vapor–liquid data obtained using the modified Colburn still are shown below. Fig. 2 and Table I show the system *n*-octane – propionic acid at atmospheric pressure. Fig. 3 and Table II show the system water – propionic acid at atmospheric pressure.

TABLE I

EXPERIMENTAL VAPOR–LIQUID EQUILIBRIUM DATA FOR PROPIONIC ACID – *n*-OCTANE AT ATMOSPHERIC PRESSURE

Temperature, °C.	Mole fraction propionic acid	
	In liquid	In vapor
125.8	0.000	0.000
125.1	0.004	0.013
124.0	0.017	0.052
122.9	0.052	0.111
122.6	0.065	0.125
121.3	0.210	0.244
121.6	0.416	0.349
123.6	0.685	0.471
127.3	0.807	0.564
130.9	0.891	0.665
136.1	0.962	0.831
137.5	0.962	0.882
138.2	0.974	0.916
139.8	0.988	0.955
141.1	1.000	1.000
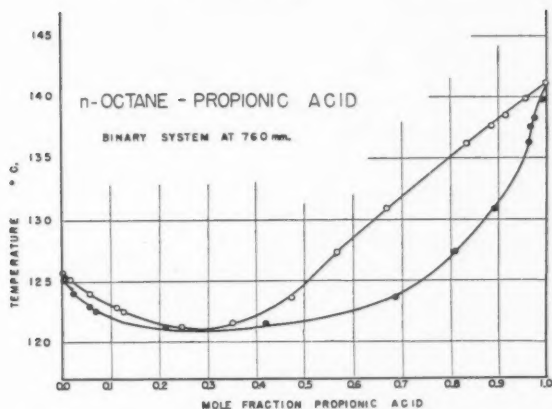
FIG. 2. System: *n*-octane – propionic acid at atmospheric pressure plotted in mole fraction.

TABLE II

EXPERIMENTAL VAPOR–LIQUID EQUILIBRIUM DATA FOR PROPIONIC ACID – WATER
AT ATMOSPHERIC PRESSURE

Temperature, °C.	Mole fraction propionic acid	
	In liquid	In vapor
100.0	0.000	0.000
100.0	0.005	0.006
99.9	0.033	0.069
99.8	0.063	0.078
100.0	0.128	0.110
101.2	0.314	0.134
103.4	0.471	0.174
106.4	0.584	0.235
110.8	0.697	0.312
115.8	0.805	0.410
122.5	0.862	0.548
126.4	0.879	0.613
130.5	0.879	0.701
135.2	0.886	0.805
138.0	0.917	0.886
141.1	1.000	1.000

The results obtained appear to be consistent. All points lie close to smooth continuous curves. A further check on the consistency of the experimental data was made by plotting on logarithmic scale the activity coefficients of the two systems against molal composition, as shown in Fig. 4. It can be seen that both curves approach the abscissa $\gamma = 1$ asymptotically as mole fraction propionic acid approaches the value unity.

FIG. 3.   System: water – propionic acid at atmospheric pressure plotted in mole fraction.
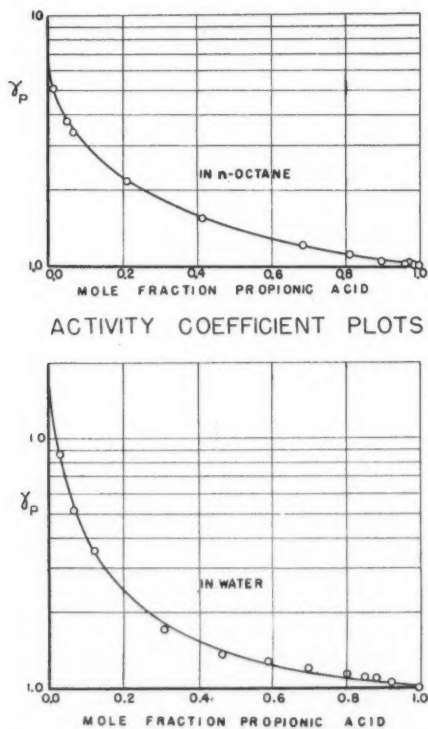
FIG. 4.   Activity coefficient of propionic acid plotted against mole fraction propionic acid in each binary system.

SOLUBILITY DATA OF THE TERNARY SYSTEM

The binodal solubility curve for the system n-octane – water – propionic acid was established by the synthetic method. In this method n-octane is titrated with water until the appearance of cloudiness. A small amount of pro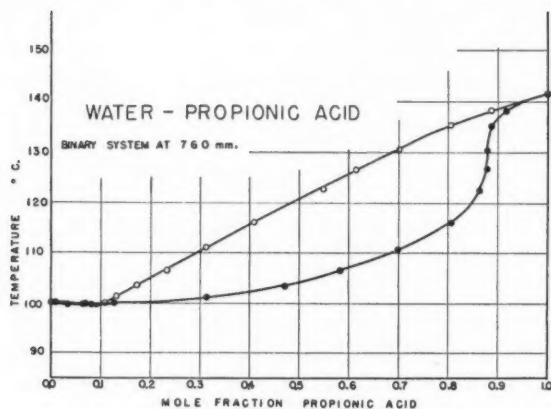pionic acid is added and the sample is again titrated to the cloudy end point with water. Each time this procedure is repeated, another point on the binodal curve is established. This procedure is repeated starting with water and titrating with n-octane and continuing as above to establish the remainder of the curve. A smooth curve is drawn through the points thus obtained. The cloudiness is caused by the appearance of two phases.

Tie-lines were determined by analyzing the two layers of mixtures of the three components lying in the two-phase region bounded by the solubility curve. Samples of each layer were pipetted from the mixture and titrated with standard base to obtain the volume fraction of propionic acid in each layer. The tie-lines were marked on a binodal curve plotted in per cent by volume in order to obtain the volume fractions of n-octane and water in each layer. The data were converted to per cent by weight. Table III lists the solubility data in weight fraction for the system n-octane – water – propionic acid.

TABLE III

SOLUBILITY DATA AT $25.0°C$. FOR SYSTEM WATER – n-OCTANE – PROPIONIC ACID
(All data are in weight fraction)

Water	n-Octane	Propionic acid
0.000	1.000	0.000
0.001	0.739	0.260
0.010	0.563	0.427
0.026	0.404	0.570
0.046	0.294	0.660
0.080	0.170	0.750
0.107	0.112	0.781
0.141	0.081	0.778
1.000	0.000	0.000
0.850	0.000	0.150
0.702	0.000	0.299
0.552	0.001	0.448
0.400	0.004	0.595
0.285	0.011	0.705
0.198	0.025	0.777
0.161	0.048	0.791

The tie-line data when plotted on an Othmer–Tobias (2) plot lay very close to a straight line, thus indicating their consistency. Table IV lists the tie-line data for the system in weight fractions.

Fig. 5 shows the solubility and tie-line data for the system plotted in weight fractions on a triangular graph.

TABLE IV

TIE-LINE DATA AT 25.0°C. FOR SYSTEM WATER – *n*-OCTANE – PROPIONIC ACID
(All data are in weight fraction)

Water-rich phase			*n*-Octane-rich phase		
Water	*n*-Octane	Propionic acid	Water	*n*-Octane	Propionic acid
0.164	0.043	0.792	0.012	0.510	0.478
0.332	0.013	0.739	0.001	0.729	0.270
0.389	0.006	0.605	0.000	0.822	0.179
0.548	0.000	0.451	0.000	0.875	0.125
0.735	0.000	0.265	0.000	0.916	0.083
0.885	0.000	0.115	0.000	0.962	0.038
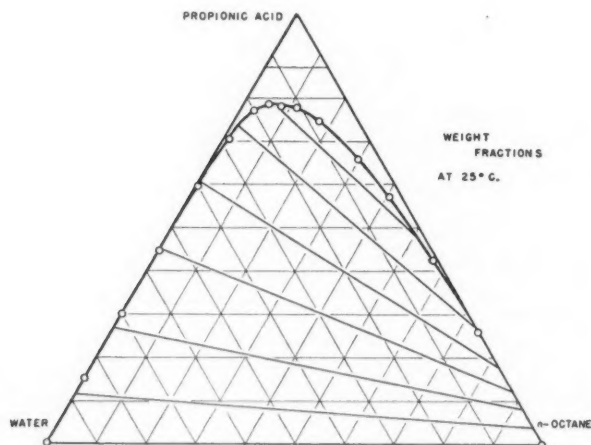
FIG. 5. Solubility and tie-line data for system: *n*-octane – water – propionic acid at 25.0°C. plotted in weight fraction.

PREDICTION OF DISTRIBUTION

The method of Scheibel and Friedland (3) was used to attempt to predict the distribution of propionic acid in the *n*-octane-rich and water-rich phases. The predicted distribution was compared with the experimentally determined distribution data. The method in brief is as follows: The experimental solubility and tie-line data were converted to mole fraction and plotted on a triangular diagram. From the activity coefficient – mole fraction graphs for propionic acid in water and in *n*-octane, values of the mole fraction of propionic acid in the binary systems *n*-octane – propionic acid and water – propionic acid for a constant value of activity coefficient were obtained. These were plotted on the triangular diagram as shown in Fig. 6. The lines of constant ternary activity coefficient for propionic acid were drawn in by the graphical method described by Scheibel and Friedland.
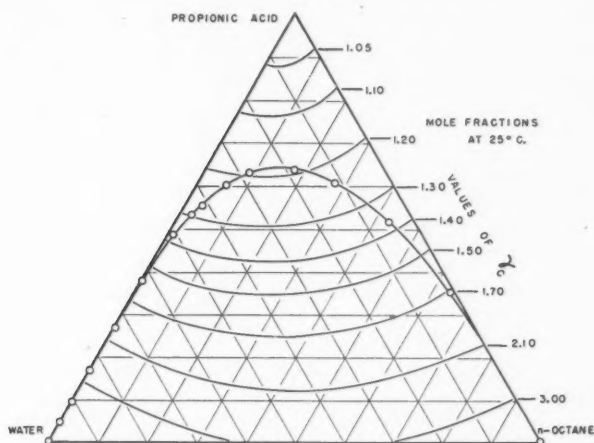
FIG. 6. Scheibel plot of ternary system at 25.0°C. plotted in mole fraction, with lines of constant ternary activity coefficient for propionic acid.

From the intersections of the lines of constant activity coefficient and the binodal curve, values of the mole fraction of propionic acid in each layer for various values of activity coefficient were obtained. From these, the activity of propionic acid in each layer for each value of activity coefficient was calculated. A plot of the activity of propionic acid in each phase against the mole
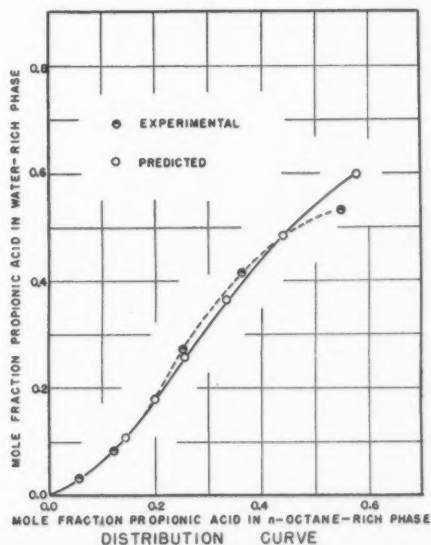
FIG. 7. Distribution of propionic acid in n-octane-rich and water-rich phases.

fraction of propionic acid was made. From this plot mole fractions of propionic acid in each phase were obtained where the activity of propionic acid in each phase was equal. With these values of mole fraction, the predicted distribution curve was drawn. Fig. 7 is a distribution curve showing the distribution of propionic acid in each of the two phases of three-component mixtures. The dotted line represents the experimental curve and the solid line is the curve predicted as described above.

The close agreement of the predicted and experimental distribution data indicates the usefulness of the Scheibel method in predicting distribution data in liquid–liquid systems using more easily available data.

CONCLUSIONS

Binary liquid–vapor equilibrium data at atmospheric pressure for the systems n-octane – propionic acid and water – propionic acid, and ternary liquid–liquid data at 25°C. for the system propionic acid – n-octane – water are reported.

The tie-lines for the ternary system were successfully predicted from the binary liquid–vapor data and the ternary solubility curve, by the method of Scheibel and Friedland.

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GRAPHICAL DISTILLATION CALCULATIONS FOR BINARY MIXTURES OF CONSTANT RELATIVE VOLATILITY[1]

By A. I. JOHNSON AND CHEN-JUNG HUANG

ABSTRACT

A graphical method for distillation calculations for binary mixtures of constant relative volatility is proposed based on the geometrical principles of similar triangles. The laborious computation of vapor–liquid equilibrium data is avoided. The assumptions and accuracy are those of the McCabe–Thiele method.

INTRODUCTION

The first mathematical treatment of the rectifying column for binary mixtures was developed by Sorel (5) in 1893. Since then several other methods (3, 6) have been proposed with simplifying assumptions. Among them the McCabe–Thiele method (1) and Ponchon (2)–Savarit (4) method are more often used in the practical design of rectifying columns because of simplicity and accuracy. The change in composition from plate to plate is calculated graphically by making material and energy balances around each plate based on the assumption that equilibrium is attained between the vapor and liquid leaving a plate. By assuming constant molal vaporization and constant molal overflow, McCabe and Thiele established a relationship between the liquid composition on the nth plate and the vapor composition from the $(n + 1)$th plate, where plates are numbered from the top, and derived the following equation for the operating line:

$$[1] \qquad y_{n+1} = \frac{R}{R + 1} x_n + \frac{1}{R + 1} x_D.$$

Then the number of theoretical plates required for rectification can be determined graphically by a stepwise method between the operating line and the equilibrium curve.

The method proposed is a modified McCabe–Thiele method for the calculation of the number of theoretical plates for the rectification of binary mixtures of constant relative volatility without plotting the equilibrium curve which requires laborious computations. The method utilizes the geometrical principles of similar triangles. Illustrations will be given for cases of infinite reflux ratio and finite reflux ratio.

GEOMETRICAL PRINCIPLES OF PROPOSED GRAPHICAL METHOD

When the relative volatility α is constant the vapor–liquid equilibrium curve can be represented mathematically as

$$[2] \qquad y = \frac{\alpha x}{1 + (\alpha - 1) x}.$$
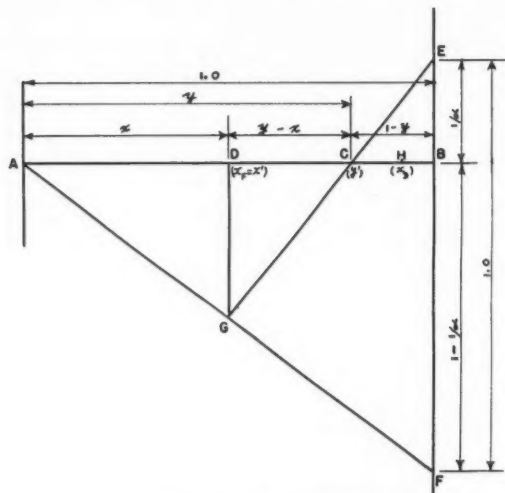
FIG. 1.   Geometrical principles of the proposed method.

In Fig. 1 the geometry of similar triangles shows that

[3] $AD/AB = DG/BF$

and

[4] $DC/DG = BC/BE,$

also

[5] $DC = AC - AD,$

[6] $BC = AB - AC.$

Combining equations [3], [4], [5], and [6]

[7] $AC = \dfrac{(AB)(AD)(BF + BE)}{(AB)(BE) + (AD)(BF)}.$

Therefore, the vapor–liquid equilibrium of binary mixtures of constant relative volatility represented by equation [2] can be established on the horizontal line of unit length AB so that

$$y = AC \quad \text{and} \quad x = AD,$$

provided that

$$AB = 1, BE = 1/\alpha, \text{ and } BF = 1 - (1/\alpha).$$

In other words, the lengths of AC and AD represent the vapor and liquid compositions at equilibrium respectively. Therefore, the operating points E and F replace the equilibrium curve on the McCabe–Thiele diagram.

METHODS FOR CALCULATION

A. Infinite Reflux Ratio

Fig. 2 illustrates the graphical calculation for rectification with total reflux. A binary mixture of constant relative volatility α equal to 2 shall be enriched so that the distillate composition x_D is equal to 0.95 and the liquid composition from the bottom x_W is equal to 0.1. The line EBF with $BE = 1/\alpha = \frac{1}{2}$ and $BF = 1 - (1/\alpha) = \frac{1}{2}$ is drawn perpendicular to the horizontal line of
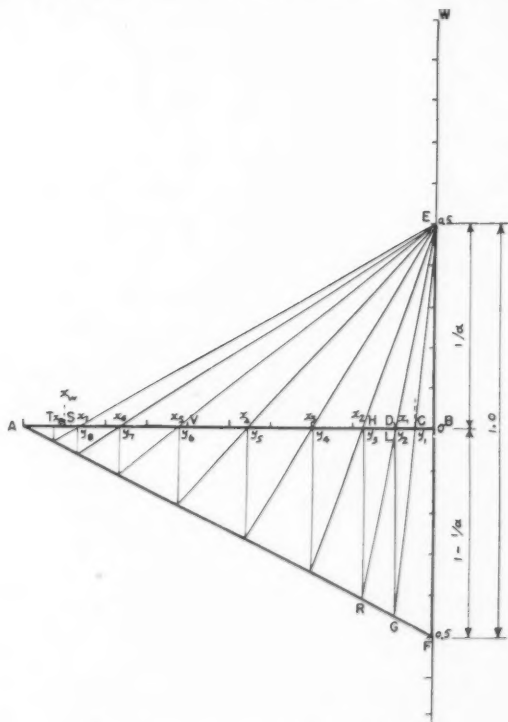
FIG. 2.   Proposed method—total reflux.

unit length AB. Distillate composition x_D, equal to the vapor composition from the top plate y_1, is located as point C on the line AB. The extension of EC intersects line AF at G, and the perpendicular line from point G reaches AB at D. Then the length of line AD represents the composition of liquid x_1, which is in equilibrium with that of vapor y_1, leaving plate 1. However, for total reflux, equation [1] can be reduced to

$$y_{n+1} = x_n,$$

that is, the composition of the vapor coming from the $(n + 1)$th plate is the same as that of liquid leaving the nth plate. Then point D represents y_2

as well as x_1. Similarly, the composition of liquid leaving plate 2 can be located at the point H by following the lines EDR and RH. By repeating the procedures the number of theoretical plates required is found to be 7.5.

B. Finite Reflux Ratio

In actual operation, distillation is carried out with a finite reflux ratio. A binary mixture of x_F equal to 0.4 with constant relative volatility α equal to 4 will be rectified so that the distillate composition x_D is equal to 0.9 while the composition of liquid from the bottom x_W is 0.1. A reflux ratio of 1.5 is adopted for the operation.

As in the case of total reflux, vertical line $WEBF$ is drawn so that $BW = EF = AB = 1$, and $BE = 1/\alpha = \frac{1}{4}$. Distillate composition x_D equal to y_1, and liquid composition from the bottom x_W, are located by the points C and S respectively.

The origins of the operating lines for rectifying and stripping sections, P and M, are established on the line AW as the intersections of the vertical
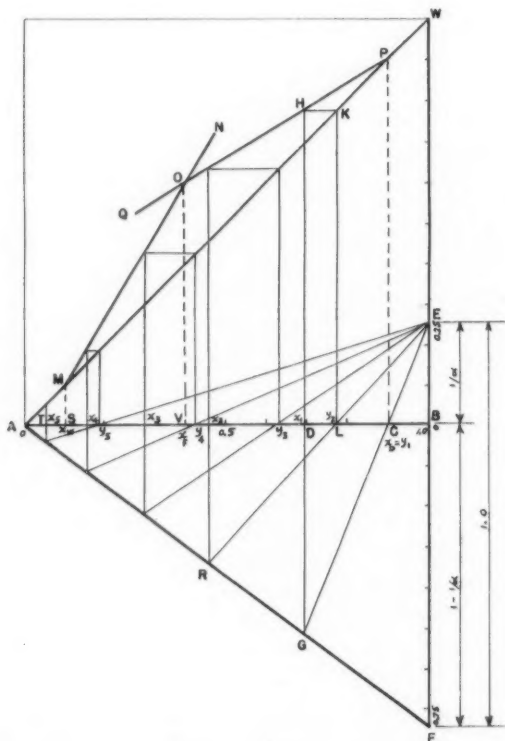

Fig. 3.   Proposed method—definite reflux.

lines through points C and S with line AW respectively. The slope of the operating line for the rectifying section with respect to a horizontal line AB is equal to $R/(R + 1)$. The intersection between the operating line and the q-line is the point O. The operating line for the stripping section can be drawn by connecting points M and O. The operating lines are drawn in the same manner as for the conventional McCabe–Thiele method. Similar to the case of total reflux, the equilibrium liquid composition x_1 corresponding to vapor composition y_1 can be located as D by following the lines ECG and GD. The extension of GD intersects the operating line PQ at H. A horizontal line through H intersects AW at K and a vertical line through K intersects AB at point L which represents the composition of vapor y_2.

This procedure is repeated for the rectifying section until the liquid composition is equal to or less than x_F. For the stripping section the procedure is similar but the operating line for the stripping section takes the place of that for the rectifying section. The operations are continued until the liquid composition is equal to or less than x_W. In this example the number of theoretical plates required is 4.6.

C. Minimum Reflux

Minimum reflux ratio R_m can be determined as

[8]
$$R_m = \frac{x_D - y'}{y' - x'}$$

where y' and x' represent the point at which the q-line intersects the vapor–liquid equilibrium curve on the McCabe–Thiele diagram.

If a liquid mixture of constant relative volatility is fed to the column at its boiling point, x' should be equal to the feed composition x_F and the corresponding y' can be located on Fig. 1 as a point C which is the intersection between EG and AB. Therefore the minimum reflux ratio R_m is the ratio of two lines CH and CD where H represents the distillate composition x_D.

The equation for the q-line is shown as follows:

[9]
$$y = \frac{q}{q - 1} x - \frac{x_F}{q - 1}.$$

For the general case, x' can be obtained by simultaneous solution of equations [2] and [9].

[10] $$x' = \frac{[q(\alpha-1)-\alpha(1-x_F)-x_F] \pm \sqrt{[q(\alpha-1)-\alpha(1-x_F)-x_F]^2+4q(\alpha-1)x_F}}{2q(\alpha-1)}.$$

Then the corresponding y' can be determined on the proposed diagram as mentioned above. Finally, the minimum reflux ratio can be calculated by substitution of x', y' in equation [8].

CONCLUSION

The proposed method is a modified McCabe–Thiele method for calculation of binary mixture of constant relative volatility utilizing the geometrical principles of similar triangles. Since the actual equilibrium curve is not

required the laborious computation and plotting of vapor–liquid equilibrium data are avoided. This advantage is particularly significant when the constant relative volatility α is not an integer. The accuracy is the same as that of the McCabe–Thiele method. The method also suggests that geometrical principles can be applied more often in chemical engineering calculations.

NOMENCLATURE

α Constant relative volatility.

q Ratio of heat required to convert 1 mole of feed to saturated vapor to molal latent heat of vaporization.

R External reflux ratio, that is, the ratio of the molal amount of reflux returned to the column to the molal amount of distillate.

x Liquid composition of binary mixture expressed in the mole fraction of more volatile component.

y Vapor composition of binary mixture expressed in the mole fraction of more volatile component.

Subscripts:

$1, 2, n, n + 1$ Plate number.
D Distillate.
F Feed.
m Minimum.
W Residue from bottom.

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